

11/16/98

JC135 U.S. PTO

FORM PTO-1082

EXPRESS MAIL LABEL NO.: EI935050979 US

PATENT

Attorney Docket No.: 30-4012

Date: November 16, 1998

BOX PATENT APPLICATION
ASSISTANT COMMISSIONER FOR PATENTS
Washington, D.C. 20231

Sir:

Transmitted herewith for filing is the patent application of:

Inventor(s): Roman RENNEKE, James C. WILLIAMS and Norm VAN DEN BUSSCHE
For: NOX REMOVAL APPARATUS INCLUDING MANGANESE DIOXIDE AND COPPER OXIDE SUPPORT

Enclosed are:

11 Pages of Specification

2 Sheets of drawing (X formal informal)

X Declaration and Power of Attorney. Will follow.

X Form PTO-1595 and an assignment of the invention to AlliedSignal Inc., of P.O. Box 1219, 101 Columbia Road
Morristown, New Jersey 07962 Will follow.

A certified copy of from which priority is claimed in the subject case pursuant to Rule 55b
and 35 U.S.C. 119. Will follow.

An associate Power of Attorney

A verified statement to establish small entity status under 37 CFR 1.9 and 37 CFR 1.27.

X Information Disclosure Statement, Form PTO 1449 and 3 prior art reference(s).

Preliminary Amendment.

General Authorization/Request to Petition for extension of time.

X Postcard

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TOTAL CLAIMS	20-20=	-0-	X 11	\$	OR	X 22	\$
INDEP CLAIMS	3-3=	-0-	X 41	\$	OR	X 82	\$
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X-Please charge my Deposit Account No. 01-1113 the amount of \$790.00 to cover the filing fees. A duplicate copy of this sheet is enclosed.

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X Any additional filing fees required under 37 CFR 1.16.

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The Commissioner is hereby authorized to charge payment of the following fees during the pendency of this application or credit any overpayment to Deposit Account No. 07-1853. A duplicate copy of this sheet is enclosed.

Any patent application processing fees required under 37 CFR 1.17.

The issue fee set in 37CFR 1.18 at or before mailing of the Notice of Allowance, pursuant to 37 CFR 1.31(b).

Any filing fees under 37 CFR 1.16 for presentation or extra claims.

Respectfully submitted,



Robert Desmond

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JC549 U.S. PTO
09/193032
11/16/98

PATENT

Docket No.: 30-4209

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Roman RENNEKE , James C. WILLIAMS and
Norm VAN DEN BUSSCHE

For: NOX REMOVAL APPARATUS INCLUDING MANGANESE
DIOXIDE AND COPPER OXIDE SUPPORT

CERTIFICATE OF MAILING

BOX PATENT APPLICATION
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

"EXPRESS MAIL" Mailing Label No.: EI935050979 US

Date of Deposit: November 16, 1998

I hereby certify that an application for patent, including:

11 pages of Specification (which includes 20 claims and a one-page Abstract); 2 Sheets of Formal drawings; an executed Combined Declaration and Power of Attorney; an executed Assignment document and Form PTO 1595, an Information Disclosure Statement, along with PTO Form 1449 and three (3) references; a Transmittal Letter (Form PTO 1082); and Return Postcard are being deposited with the U.S. Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Box Patent Application, Washington, D.C. 20231.

Date of Deposit: 16 November 1998

Robert Desmond
Robert Desmond

PATENT
Docket No. 30-4012

**NO_x REMOVAL APPARATUS INCLUDING MANGANESE DIOXIDE AND
COPPER OXIDE SUPPORT**

This application claims the benefit of provisional application no. 60/066,146 filed
5 on November 19, 1997.

BACKGROUND OF THE INVENTION

The present invention relates to NO_x removal. More specifically, the invention
relates to an adsorbent for removing nitric oxide (NO) and nitrogen dioxide (NO₂) from a
10 gas such as air.

NO_x removals systems are commonly used in applications ranging from air
filtration to auto emission control. U.S. Patent No. 5,362,463 discloses a NO_x
adsorbent including a support made of a mixture of manganese oxide and aluminum
oxide. Between 20 percent and 80 percent manganese oxide is used, with the
15 remainder being aluminum oxide. The adsorbent further includes an alkali material
such as potassium carbonate. The '463 patent discloses that potassium is used in
amounts ranging between five and fifty percent. As air flows over the adsorbent, NO_x is
removed.

NO_x removal is performed at high air temperatures. The air temperature
exceeds 200°C. According to the '463 patent, there are temperature limitations on the
20 removal of the NO_x at air temperatures below 100°C.

It would be desirable to removal NO_x at temperatures below 100°C.

SUMMARY OF THE INVENTION

NO_x is removed at lower temperatures by an apparatus according to the present
invention. The apparatus includes a support made of a mixture including manganese
dioxide and copper oxide; and an alkali material combined with the support. The
support and the alkali material are combined for NO_x removal. The apparatus can
25 remove NO_x from a gas such as air at temperatures below 100°C. The apparatus has
a high NO_x removal capacity, and it is durable to air and thermal exposure.

According to different aspects of the invention, the support may be impregnated with the alkali material, the support and the alkali material may be formed as separate particles that are mixed together, or the support and the alkali material may be formed as separate particles that are placed in separate vessels.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an illustration of a NOx removal system according to the present invention;

10 Figure 2 is an illustration of a method of forming an adsorbent for the NOx removal system according to the present invention; and

Figure 3 is an illustration of an alternative NOx removal system according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

15 Figure 1 shows a NOx removal system 10 including a vessel 12 containing an adsorbent 14. The vessel 12 is contained within an enclosure 16. During NOx removal, an incoming stream 18 of gas such as air is flowed over the adsorbent 14. The
20 adsorbent 14 reduces the levels of nitric oxide (NO) and nitrogen dioxide (NO₂) in the gas. Leaving the vessel 12 is a stream 20 of gas having reduced levels of nitric oxide and nitrogen dioxide.

The adsorbent 14 can remove the NOx in gas having a temperature above 100°C. However, the adsorbent 14 can also remove NOx in gas having a temperature
25 below 100°C. The adsorbent 14 can even remove NOx in a gas having a temperature of 35°C or perhaps lower than 20°C. Thus, the adsorbent 14 can remove NOx at low temperatures.

The incoming gas 18 may be heated or cooled to a temperature at which NOx removal occurs (the "operating" temperature). If, however, the gas is already at a
30 desirable operating temperature, then a separate heater or cooler is not used. For example, the enclosure 16 is a vehicle including a combustion engine, and it is desired

to remove NO_x in exhaust gas from the combustion engine. The exhaust gas from the combustion engine is already heated. Thus, the exhaust gas from the combustion engine could be flowed directly over the adsorbent 14.

The adsorbent 14 includes two components: an alkali material, and a support for the alkali material. The support is a mixture including manganese dioxide (MnO₂) and copper oxide (CuO). At least about sixty weight percent (60 wt%) manganese dioxide is included in the mixture, and at least about ten weight percent (10 wt%) copper oxide is included in the mixture. The support may be made of commercially available mixtures such as "CARULITE 200" (available from Carus Chemical Co. located in Peru, Illinois) and "HOPCALITE" (available from Strem Chemicals located in Newburyport, Massachusetts). The "CARULITE 200" mixture includes about sixty to seventy five weight percent manganese dioxide (60 wt% to 75 wt% MnO₂), about eleven to fourteen weight percent copper oxide (11 wt% to 14 wt% CuO), and about fifteen to sixteen weight percent aluminum oxide (15 wt% to 16 wt% Al₂O₃). The "HOPCALITE" mixture includes at least seventy weight percent manganese dioxide (70 wt% MnO₂) and at least ten percent copper oxide (10 wt% CuO). No aluminum oxide is believed to be present. In addition to supporting the alkali material, the support performs a function of oxidizing the nitric oxide into nitrogen dioxide.

The support mixture may be formed as particles that are porous. The porous support particles may have a high internal surface area of at least 150 meters²/gram. The geometry of the support particles may be pellets, granules, cylinders, spheres, extrudates, powders, etc. The support particles may have a size as large as five (5) millimeters. It has been found that smaller particles exhibit better gas diffusion and removal efficiency than larger particles.

The alkali material may be potassium carbonate (K₂CO₃). The alkali material removes the nitrogen dioxide by a chemical reaction, which generates nitrate and/or nitrite on the adsorbent's exposed surface. The adsorbent 14 includes about three to forty weight percent potassium carbonate (3 wt% to 40 wt% K₂CO₃), with the remainder being the support.

The alkali material may instead be potassium hydroxide (KOH) or another alkali or alkaline-earth carbonate or hydroxide. For example, carbonates of calcium (Ca), lithium (Li), sodium (Na), rubidium (Rb), or cesium (Cs) may be used.

Separate tests have been conducted on adsorbents 14 including "CARULITE 200" particles and "HOPCALITE" particles, and it has been found that both adsorbents work well on air having temperatures between 21°C and 450°C. Efficiency of the NO_x removal increases as the temperature is increased. This temperature dependence is more pronounced with the nitric oxide than with the nitrogen dioxide.

Optimal loading of the potassium carbonate has been found to vary in proportion to the operating temperature of the gas. For an operating temperature of 50°C, an optimal loading of potassium carbonate has been found to be in the range of three weight percent to twelve weight percent (3 wt% to 12 wt% K₂CO₃), and preferably ten weight percent (10 wt%). For an operating temperature of 250°C, an optimal loading of potassium carbonate has been found to be between twenty weight percent and forty weight percent (20 wt% and 40 wt% K₂CO₃), and preferably thirty weight percent (30 wt%). For temperatures between 50°C and 250°C, the weight percent of the potassium carbonate could be interpolated.

The alkali material may be combined with the support in different ways. For example, inert support particles could be coated with the alkali material, and the coated inert particles could be uniformly dispersed in the vessel 12 with the support particles (e.g., the "CARULITE 200" particles or "HOPCALITE" particles). The inert particles for the alkali material could be high surface area alumina particles as well as particles such as silica, titania and zirconia. The inert particles also have a high internal surface area for dispersion of the alkali material. The surface area may be above about 10 meters²/gram.

In the alternative, the support and alkali may be layered within the vessel 12. For example, the support particles may be placed in front of inert particles that are coated with alkali material.

Figure 2 illustrates yet another way in which the support and alkali material may be combined. The support particles (e.g., the "CARULITE 200" particles or "HOPCALITE" particles) may instead be coated or impregnated with the alkali material.

The support particles may be procured from a commercial manufacturer or produced by mixing together the manganese dioxide and copper oxide (block 100). The support particles may be produced by starting with a mixture of water soluble salts of manganese and copper, followed by precipitation and calcining.

5 An additional material such as chromium oxide may optionally be added to the support mixture (block 102). The chromium oxide may be added, for example, by impregnating the support mixture with water soluble chromium salt, or mixing the water soluble chromium salt with the water soluble salts of manganese and copper.

10 The support particles may then be impregnated with the alkali material by forming an aqueous solution of the alkali material (block 104), impregnating the support particles with the aqueous solution (block 106), and drying the impregnated support particles (block 108). Impregnating the support particles with the aqueous solution allows direct physical contact between the support particles and the alkali material because the alkali material is deposited on the support particles.

15 After being dried, the impregnated support particles may also be heat treated at a temperature above the expected operating temperature of the gas (block 110). If, however, the impregnated particles are dried at a temperature above the expected operating temperature of the air, the heat treatment step (block 110) may be skipped.

20 Such an absorbent may be formed, for example, by combining 10 wt% potassium carbonate (K_2CO_3) with "CARULITE 200" particles. These two components are combined by impregnating 100 grams of commercially available "CARULITE 200" particles with 70 mL of an aqueous solution of K_2CO_3 containing 11 grams of K_2CO_3 . The impregnated support particles are then dried in a rotary impregnator at a temperature of 100°C. Both the "CARULITE 200" particles (prior to impregnation) and
25 the dried particles (after impregnation) are sieved to 20-35 Tyler mesh.

 Figure 3 shows yet another way in which the support and alkali material may be combined. A first vessel 200 containing the support 202 (e.g., "CARULITE 200" particles) is followed by a second vessel 204 containing the alkali material on inert particles 206. During NO_x removal, a stream 208 of gas is passed over the support 202
30 in the first vessel 200. A gas stream 210 leaving the first vessel 200 bed is then passed

over the alkali material in the second vessel 204. A gas stream 212 leaving the second vessel 204 has reduced levels of nitric oxide and nitrogen dioxide.

Still another way of combining the support and alkali would be to place the support 202 in the first vessel 200 and the alkali-coated support 14 in the second
5 vessel 204.

Thus disclosed is an adsorbent that can remove NO_x in a gas having a temperature below 100°C. The adsorbent can reduce the problems associated with raising the temperature of the gas prior to NO_x removal. In certain instances, the adsorbent might allow a heater to be eliminated. In other instances, the adsorbent
10 might be placed in a more convenient location inside the enclosure. For example, if the gas stream temperature varies at different locations within the enclosure, the invention will afford greater flexibility in placing the adsorbent along the gas stream, especially if the gas stream temperature is below 100°C at certain locations.

The adsorbent has been found to exhibit high air exposure and thermal durability. Resulting is an adsorbent having a long lifetime.

The adsorbent is also believed to have a higher NO_x adsorption capacity. The higher adsorption capacity allows the adsorbent to be used for longer periods before the adsorbent becomes saturated. After the adsorbent becomes saturated, it could be discarded. In the alternative, the adsorbent could be regenerated. Still, the longer
20 lifetime of the adsorbent would reduce the frequency of regeneration.

The invention may be used, without limitation, for the removal of NO_x from breathable air; the removal of NO_x from combustion engine exhaust; the removal of NO_x from gas streams generated by coal and residual oil burning furnaces; the removal of NO_x from catalytic oxidizers and non-catalytic thermal oxidizers that process
25 nitrogen-containing organic molecules such as amines; the removal of NO_x from nitric acid production plants; and the removal of NO_x from nitrite production plants. During the NO_x removal, oxygen should be present.

Design considerations such as adsorbent size, gas flow rate, and desired NO_x levels in the effluent gas will depend upon the application for which the NO_x removal
30 system is intended.

PATENT
Docket No. 30-4012

The present invention is not limited to the specific embodiments described above. Instead, the present invention is construed according to the claims that follow.

WHAT IS CLAIMED IS:

1. NOx removal apparatus comprising:
a support made of a mixture including manganese dioxide and copper oxide; and
an alkali material combined with the support;
the support and the alkali material being combined for NOx removal.
2. The apparatus of claim 1, wherein the support includes at least about sixty weight percent manganese dioxide and at least about ten weight percent copper oxide.
3. The apparatus of claim 1, wherein the alkali material is potassium carbonate, the potassium carbonate being between about 3 weight percent and 40 weight percent of the combined support and alkali material.
4. The apparatus of claim 1, wherein the alkali material is potassium carbonate, the potassium carbonate being between about 3 weight percent and 12 weight percent of the combined support and alkali material.
5. The apparatus of claim 1, wherein the alkali material is potassium carbonate, the potassium carbonate being between about 20 weight percent and 40 weight percent of the combined support and alkali material.
6. The apparatus of claim 1, wherein the support particles have an internal surface area of at least 150 meters²/gram.
7. The apparatus of claim 1, wherein the support is impregnated with the alkali material.

8. The apparatus of claim 1, wherein a first group of particles is made of the support, and wherein the alkali material is on a second group of particles, and wherein the first and second groups of particles are mixed together.

9. The apparatus of claim 1, wherein a first vessel contains the support, wherein a second vessel contains the alkali material, and wherein air is flowed over the support and then the alkali material during NO_x removal.

10. The apparatus of claim 1, further comprising an enclosure for providing a gas to the support and alkali material, the gas having a temperature below 100°C during NO_x removal.

11. An adsorbent for removing NO_x from a gas, the adsorbent comprising:
support particles made of a mixture including manganese dioxide and copper oxide; and
an alkali material;
the support particles being impregnated with the alkali material.

12. The adsorbent of claim 11, wherein the support includes at least about sixty weight percent manganese oxide and at least about ten weight percent copper oxide.

13. The adsorbent of claim 11, wherein the mixture further includes chromium oxide.

14. The adsorbent of claim 11, wherein the alkali material is potassium carbonate, the potassium carbonate being between about 3 weight percent and 40 weight percent of the adsorbent.

15. The adsorbent of claim 11, wherein the alkali material is potassium carbonate, the potassium carbonate being between about 3 weight percent and 12 weight percent of the adsorbent.

16. The adsorbent of claim 11, wherein the alkali material is potassium carbonate, the potassium carbonate being between about 20 weight percent and 40 weight percent of the adsorbent.

17. The adsorbent of claim 11, wherein the support particles have an internal surface area of at least 150 meters²/gram.

18. A method of removing NO_x from a gas having a temperature below 100°C, the method comprising the steps of:

exposing the gas to porous particles made of a mixture including manganese dioxide and copper oxide; and

exposing the gas to an alkali material.

19. The method of claim 18, wherein the gas is exposed to the alkali material in a common vessel.

20. The method of claim 18, wherein the gas is exposed first to the mixture and then to the alkali material, the mixture and the alkali material being contained in separate vessels.

NO_x REMOVAL APPARATUS INCLUDING MANGANESE DIOXIDE AND COPPER OXIDE SUPPORT

5 ABSTRACT OF THE DISCLOSURE

Nitric oxide (NO) and nitrogen dioxide (NO₂) are removed from air by an adsorbent including a combination of a support and an alkali material. The support is a mixture including manganese dioxide (MnO₂) and copper oxide (CuO). The alkali material may be, for example, potassium carbonate (K₂CO₃) or potassium hydroxide (KOH). The
10 adsorbent allows efficient NO_x removal occurs at temperatures below 100°C.

FIGURE 1

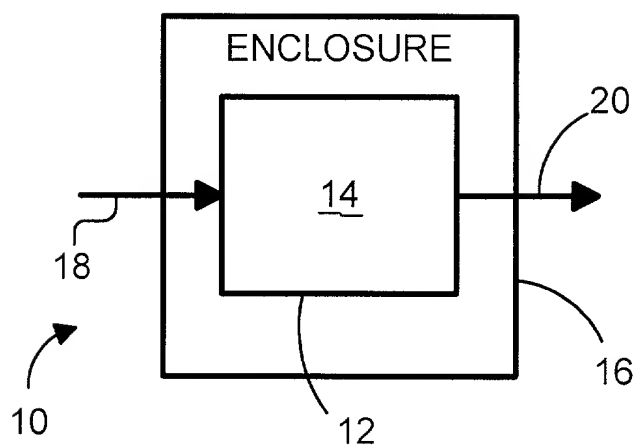


FIGURE 3

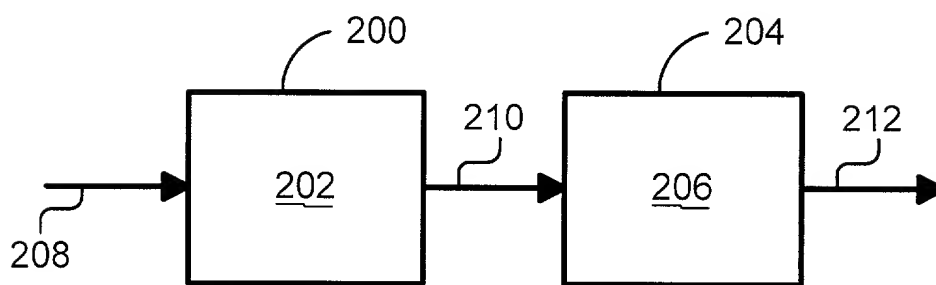
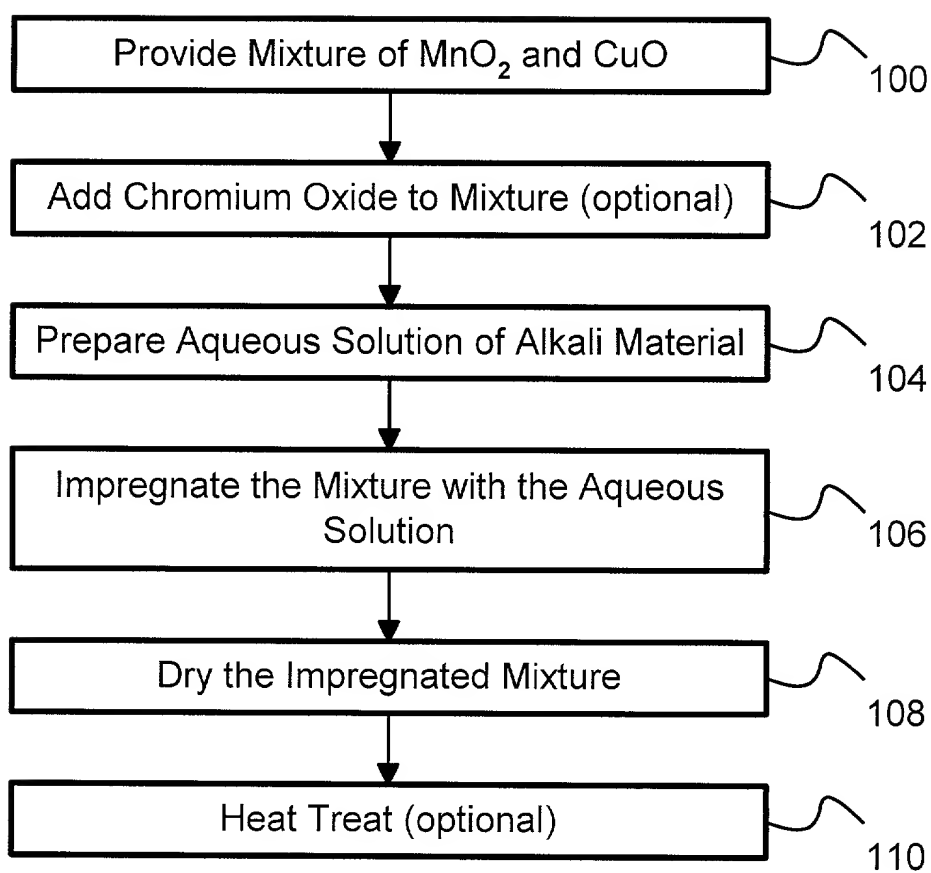


FIGURE 2



DECLARATION FOR PATENT APPLICATION

Docket Number (Optional)
30-4012

As a below named inventor, I hereby declare that.

My residence, post office address and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if Plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

NOX REMOVAL APPARATUS INCLUDING MANGANESE DIOXIDE AND COPPER OXIDE SUPPORT

Is attached hereto unless the following box is checked

☐ was filed on _____ As United States Application Number or PCT International Application Number _____ And was amended on _____ (If applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims as Amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

(Number)	(Country)	(Day/Month/Year Filed)
Number	(Country)	Day/Month/Year Filed

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below

67066,146	November 19, 1997
(Application Number)	(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this

Application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of this prior application and the national or PCT International filing date of this application

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
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(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
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I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information And belief are believed to be true; and further that these statements were made with the knowledge that willful false statements like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and That such willful false statements may jeopardize the validity of the application or any patent issued thereon

Full name of sole or first inventor (given name, family name) Roman Renneke

Inventor's signature Roman T. Renneke Date November 13, 1998

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☐ Additional inventors are being named on separately numbered sheets attached hereto

SECOND PAGE OF DECLARATION FOR PATENT APPLICATION

Docket No.: 30-4012

Inventor's Signature:

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11/13/98

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Inventor's Signature:

Date:

Name of Fourth Inventor:

Residence:

Citizenship:

P.O. Address:

Inventor's Signature:

Date:

Name of Fifth Inventor:

Residence:

Citizenship:

P.O. Address:

Inventor's Signature:

Date:

Name of Sixth Inventor:

Residence:

Citizenship:

P.O. Address:

Inventor's Signature:

Date:

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Residence:

Citizenship:

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